

**Tetrakis(trifluoroacetoxymcuri)methane and Tetrakis(acetoxymcuri)-methane as the Reaction Products of Hofmann's Base with the Corresponding Acid: X-Ray Crystallographic Evidence**

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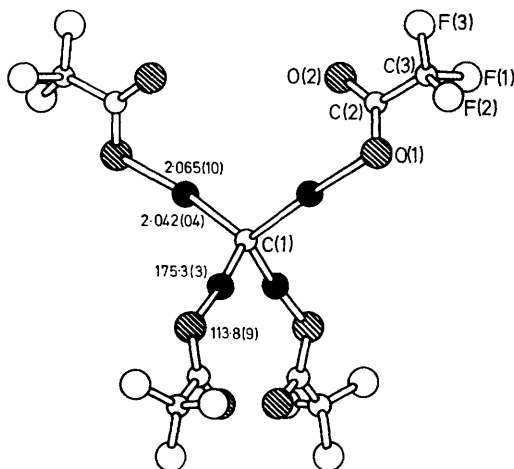
*Summary* It has been shown by X-ray structure analysis that the crystals obtained from the solution of ethane hexamercarbide (Hofmann's base) in trifluoroacetic or acetic acid are tetrakis(trifluoroacetoxymcuri)methane,  $C(HgOCOCF_3)_4$ , and tetrakis(acetoxymcuri)methane,  $C(HgOCOCH_3)_4$ , respectively.

THE compound obtained by mercuration of ethanol with mercuric oxide in alkali has been formulated as a derivative of the permercurated ethane,  $C_2Hg_6(OH)_2$ , and is known as

ethane hexamercarbide.<sup>1</sup> With nitric, sulphuric and perchloric acid it forms salts from which the original hexamercarbide is regenerated by alkalis. The anion-exchange properties of ethane hexamercarbide indicated its polymeric structure which also explained its insolubility in all solvents.<sup>2</sup> By analogy with Millon's base<sup>3</sup> we propose the name Hofmann's base for ethane hexamercarbide.<sup>4</sup>

Hofmann's base was found to dissolve completely in aqueous carboxylic acids. The crystalline compounds obtained from the solutions were not the carboxylates of

Hofmann's base but the carboxy-derivatives of permercurated methane  $C(HgOCOCF_3)_4$  and  $C(HgOCOCH_3)_4$  whose formulae were confirmed by structure analysis. Consequently, Hofmann's base is a methane derivative and can be formulated as the hydroxide of a polymeric oxonium ion containing  $C-Hg-(OH)^+-Hg-C$  bridges formed by condensation from hydroxide  $C(HgOH)_4$ , the final mercuriation



FIGURE

product of ethanol. These oxonium bridges are not affected by oxo-acids which give ionic salts (*e.g.*, nitric or perchloric acid) but are split by acids which form covalent salts with mercury (*e.g.*, carboxylic acids). From carboxy-derivatives Hofmann's base is also regenerated by alkalis. Our study of Hofmann's base and its salts will be published shortly elsewhere.

*Crystal data:* Tetrakis(trifluoroacetoxymercuri)methane,  $C(HgOCOCF_3)_4$ , tetragonal crystals, space group  $P4_2/n$ ,  $a = 12.866(4)$ ,  $c = 6.111(2)$  Å,  $V = 1011.6$  Å<sup>3</sup>,  $D_m = 4.06$  g cm<sup>-3</sup>,  $Z = 2$ ,  $D_c = 4.15$  g cm<sup>-3</sup>,  $\mu = 309.7$  cm<sup>-1</sup>. 888 non-zero independent reflections were collected on Philips PW 1100 diffractometer using Mo- $K_\alpha$  radiation. The structure

was solved by conventional heavy atom methods and refined anisotropically to  $R = 0.028$  (Figure).

The crystals consist of discrete  $C(HgOCOCF_3)_4$  molecules with symmetry as shown in the Figure. The carbon atom C(1) is bonded to four mercury atoms in an almost regular tetrahedron, the tetrahedral angles being 112.36(2) and 108.36(2)°, respectively. The bond lengths are given in the Figure. Each mercury atom is linked to one carboxyloxy oxygen atom at 2.065(10) Å while the second oxygen atom from the same carboxyl group is 2.984(12) Å away from mercury, as found in other organomercurials.<sup>5</sup> The geometry of the trifluoroacetoxy group agrees with the known data.

Tetrakis(acetoxymercuri)methane,  $C(HgOCOCH_3)_4$ , needle-shaped monoclinic crystals, space group  $P2_1/c$ ,  $a = 7.262(7)$ ,  $b = 21.816(12)$ ,  $c = 12.003(8)$  Å,  $\beta = 98.8(8)^\circ$ ,  $V = 1899.2$  Å<sup>3</sup>,  $D_m = 3.70$  g cm<sup>-3</sup>,  $Z = 4$ ,  $D_c = 3.71$  g cm<sup>-3</sup>,  $\mu = 618.7$  cm<sup>-1</sup>. Diffraction data were collected on an integrating Weissenberg camera (multiple-film technique) using Cu- $K_\alpha$  radiation. 1830 Independent reflections were measured by means of a microdensitometer. The structure was solved by the Patterson and Fourier method and refined by least-squares procedure assuming anisotropic temperature factor for mercury and isotropic temperature factor for all other non-hydrogen atoms to a current  $R$  value of 0.114.

The molecular geometry of  $C(HgOCOCH_3)_4$  is very similar to that found for the trifluoroacetoxy compound. At the present stage of the analysis the C-Hg bond lengths are from 2.03 to 2.07 Å and the tetrahedral angles from 106 to 112°. The bonds at the mercury atom are nearly collinear, with Hg-O bond lengths from 2.02 to 2.18 Å.

The physical properties and chemical reactions of the crystals correspond to those of tetrakis(acetoxymercuri)methane obtained previously by a completely different method.<sup>6</sup>

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